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Molecular Complex of Cadmium(II) Trifluoroacetate with Triphenylphosphine: Crystal Structure and Luminescence Properties

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Abstract—Cadmium compound $[Cd(CF_3COO)_2(Ph_3P)_2]$ is synthesized, and its crystal structure is determined. The crystals are monoclinic: space group $C2/c$, $a = 20.318(4)$, $b = 10.432(2)$, $c = 18.661(4)$ Å, $\beta = 104.18(1)°$, $V = 3834.8(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.495$ g/cm^3. The Cd atom arranged on the 2-fold crystallographic axis has a distorted octahedral coordination due to four oxygen atoms of crystallographically equivalent trifluoroacetate ligands and two phosphorus atoms of triphenylphosphine. Each fluorine atom of the trifluoroacetate groups is randomly disordered over three equally probable positions. The compound is luminescent.

Keywords: cadmium trifluoroacetate, triphenylphosphine, structure, luminescence

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INTRODUCTION

Phosphine ligands continue to play a serious role in the coordination and organoelement chemistry of transition *d* metals, which are widely used in catalysis [1]. Elements of the main subgroups also form complexes with phosphines, although the studies of these elements are met much rarely [2]. The phosphine complexes of Zn(II), Cd(II), and Hg(II) have been known long ago. However, the later works mainly concern the Zn(II) and Hg(II) compounds. The main types of the cadmium complexes with phosphines have been established earlier, but only a few works appeared recently [2]. Since cadmium is widely applied in industrial units and possesses toxic properties, great attention is given to the removal of Cd from aqueous media, in particular, using the phosphorus-containing organic derivatives [3]. The cadmium salts with these ligands form both discrete and dimeric compounds with the tetrahedral and pentacoordinated environment of Cd(II) [4–10].

It is known that the compositions and structures of the Cd(II) phosphine complexes depend on the nature of counterions and volume characteristics of phosphines. As a rule, the halide complexes have the $CdHal_2(Ph_3P)_2$ and $Cd_2Hal_4(Ph_3P)_2$ compositions with the distorted tetrahedral environment of the metal ion. The Cd^{2+} ion is characterized by the octahedral structure in $Cd[P(cyclo\text{-}C_6H_{11})_3]_2(NO_3)_2 \cdot CH_2Cl_2$ with aliphatic phosphine and NO_3 group. The polymeric structure is observed in compound $CdCl_2(PhMe_2P)$ with the bridging chlorine atoms and pentacoordination environment of the central atom as a trigonal bipyramid. When the chelate anion is used in compound $Cd(Et_2NCS_2)_2PEt_3$, the environment of the Cd^{2+} ion is a distorted tetragonal pyramid. Data on the Cd(II) complexes containing simultaneously triphenylphosphine and carboxylate groups are restricted only by the data on the synthesis and structure of $[Cd(CF_3COO)_2(Ph_3P)]_2$, which is dimeric due to the bridging function of the trifluoroacetate anions [11, 12]. It is known that the character of coordination of the carboxylate anions depends on the nature of the donor ligands that coexist in the internal sphere of the metal. It can be assumed that the change in the conditions of the reaction of Cd(II) trifluoroacetate with PPh_3 would result in the formation of the complex with another type of coordination of trifluoroacetate anions.

Compound $[Cd(CF_3COO)_2(Ph_3P)]_2$ was synthesized in ethanol at the equimolar ratio of cadmium trifluoroacetate to Ph_3P [11, 12]. In this work, the reaction of cadmium trifluoroacetate with Ph_3P in acetonitrile at the Cd(II) to PPh_3 ratio equal to 1 : 2 afforded complex $[Cd(CF_3COO)_2(Ph_3P)_2]$ (**I**), which was studied by X-ray structure analysis and photoluminescence (PL).

EXPERIMENTAL

Cadmium hydroxide, triphenylphosphine (reagent grade), and 99% trifluoroacetic acid (Merck) were used. Cadmium trifluoroacetate was prepared by the heating of a suspension of $Cd(OH)_2$ with CF_3COOH (ratio 1 : 2) in an aqueous-alcohol (1 : 1) solution in a water bath until the hydroxide was dissolved. The procedure was followed by filtration and filtrate evaporation to the syrup consistence. After cooling the crystallized product was triturated, heated in vacuo at 110–120°C for 60 min, and analyzed. The obtained compound corresponded to the composition $Cd(CF_3CO_2)_2 \cdot 0.25H_2O$ (found, %: C, 14.08; calculated, %: C, 14.08).

Synthesis of compound I. Trifluoroacetate (0.30 g, 0.88 mmol) was dissolved in acetonitrile (10 mL), and triphenylphosphine (0.46 g, 1.75 mmol) was dissolved in CH_3CN (10 mL). The solutions were mixed, and the mixture was kept for 1.5 h. Then the first portion of the isolated solid phase was decanted from the solution but was not studied further because it was not suitable for X-ray structure analysis. The crystals were obtained from the mother liquor by slow evaporation, separated from the solution, washed with acetonitrile, and dried in air. The yield of compound **I** was 40%. The crystals corresponded to the composition $[Cd(CF_3COO)_2(Ph_3P)_2]$.

For $C_{40}H_{30}F_6O_4P_2Cd$ (**I**)		
Anal. calcd., %	C, 55.55	H, 3.49
Found, %	C, 55.74	H, 3.57

X-ray structure analysis of compound **I** was carried out on an Enraf-Nonius CAD-4 automated diffractometer. The structure was solved by a direct method (SHELXS-97) [13] and refined by least squares in the full-matrix anisotropic approximation for all nonhydrogen atoms (SHELXL-97) [14]. Positions of the hydrogen atoms were calculated geometrically and included into the refinement by the riding model with fixed isotropic temperature parameters. The main experimental characteristics and unit cell parameters are presented in Table 1. Selected bond lengths and bond angles are given in Table 2.

The crystallographic data for the structure of compound **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file no. CCDC 1879877; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

The PL spectra of compound **I** were recorded at room temperature on a PE LS-55 spectrometer (the resolution was 0.5 nm, and the gap width was varied from 7 to 10 nm) using an attachment for solid-state samples.

RESULTS AND DISCUSSION

In the structure of compound **I**, the Cd atom arranged on the 2-fold crystallographic axis has the octahedral coordination due to four oxygen atoms of the equivalent chelate trifluoroacetate ligands and two crystallographically equivalent phosphorus atoms of triphenylphosphine (Cd(1)–O(1) 2.293(1), Cd(1)–$O(1)^{\#1}$ 2.293(1), Cd(1)–O(2) 2.613(4), Cd(1)–$O(2)^{\#1}$ 2.613(4), Cd(1)–P(1) 2.590(1), Cd(1)–$P(1)^{\#1}$ 2.590(1) Å; for the angles at the Cd(II) atom, see Table 2). Octahedral complex **I** is formed as a result of the interaction of the ligands (Fig. 1). The fluorine atoms of trifluoroacetate are randomly disordered over three positions each ($C(20)–F_{average}$ 1.35 ± 0.01 Å). Note that the trifluoroacetate ion is weakly bound to the Cd^{2+} ions (Cd–O(2) 2.613(4) Å). The minimum O(1)Cd(1)O(2) angle is 52.5(1)°, and the maximum $P(1)Cd(1)O(2)^{\#1}$ angle is 146.18(9)° (Table 2). Probably, this orientation of the ligands induces a noticeable distortion of the coordination polyhedron of the Cd^{2+} ion.

Note that the structures of compound **I** with aromatic phosphine and $Cd[P(c\text{-}C_6H_{11})_3]_2(NO_3)_2 \cdot CH_2Cl_2$ (**II**) with aliphatic phosphine have similar crystallographic characteristics and structures of the coordination polyhedron of the Cd^{2+} ion in spite of different compositions. In compound **II**, the Cd^{2+} ion also lies on the 2-fold crystallographic axis and has the octahedral environment due to four O atoms of two equivalent bidentate nitrate ions (Cd–O(1) 2.575(8) Å and Cd–O(2) 2.405(9) Å) and two equivalent P atoms of aliphatic phosphines (Cd–P 2.602(2) Å). The Cd–P distances are close: 2.590(1) Å (**I**) and 2.602(2) Å (**II**). The PCdP angles are 122.12(5)° (**I**) and 139.56(9)° (**II**).

The PL spectrum of compound **I** contains an intense peak at 485 nm caused by the electronic transitions inside the triphenylphosphine ligands (Fig. 2). Free PPh_3 luminesces at 500 [15] and 447 nm [16]. The coordination of PPh_3 to the metal ions induces bands at 487, 513, and 455 nm in the PL spectra of $Ag(PPh_3)_2L$ (L is *p*-toluenesulfonate) [16], $Au(PPh_3)_2L$ [15], and $Cd(PPh_3)_2Cl_2$ [17], respectively.

Thus, we synthesized the second cadmium compound $[Cd(CF_3COO)_2(Ph_3P)_2]$ (Cd : P = 1 : 2) containing simultaneously the carboxylate anion and triphenylphosphine in the internal sphere. In this compound, the carboxylate anion manifests the chelate properties, unlike $[Cd(CF_3COO)_2(Ph_3P)]_2$ (Cd : P = 1 : 1) [11, 12] in which the carboxylate anion is the bridging ligand.

FUNDING

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Table 1. Crystallographic data and the main experimental characteristics for the structure of compound **I**

Parameter	Value
FW	862.98
Color, habitus	Yellow, block
Crystal size, mm	0.18 × 0.16 × 0.09
Crystal system; space group	Monoclinic; *C*2/*c*
Cell parameters:	
a, Å	20.318(4)
b, Å	10.432(2)
c, Å	18.661(4)
β, deg	104.18(3)
V, Å^3	3834.8(13)
Z	4
ρ_{calcd}, g/cm^3	1.495
μ_{Mo}, mm^{-1}	0.722
F(000)	1736
T, K	293(2)
Radiation (λ, Å)	MoK_α (1.71073)
Scan mode	ω
θ Range, deg	2.07–26.96
Ranges of indices	$-24 \le h \le 24$, $-12 \le k \le 1$, $-22 \le l \le 1$
Total number of reflections/independent (R_{int})	4588/3768 (0.0291)
Completeness for θ = 26°, %	100
Number of reflections with $I \ge 2\sigma(I)$	2362
Absorption correction	Semiempirical, by equivalents
T_{min}/T_{max}	0.8811/0.9313
Number of refined parameters	252
GOOF for F^2	1.031
R ($I \ge 2\sigma(I)$)	$R_1 = 0.0356$, $wR_2 = 0.0899$
R (all data)	$R_1 = 0.0917$, $wR_2 = 0.1053$
Residual electron density (max/min), e/Å^3	0.612, –0.548

Table 2. Selected bond lengths (Å) and bond angles (deg) in the structure of compound **I***

Bond	*d*, Å	Bond	*d*, Å
Cd(1)–O(1)	2.293(3)	Cd(1)–O(2)	2.613(4)
Cd(1)–P(1)	2.590(1)		
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)Cd(1)O(1)$^{\#1}$	139.6(2)	P(1)Cd(1)O(2)$^{\#1}$	146.18(9)
O(1)Cd(1)P(1)$^{\#1}$	97.64(9)	O(1)Cd(1)O(2)	52.50(12)
O(1)Cd(1)P(1)	101.61(9)	P(1)$^{\#1}$Cd(1)O(2)	146.18(9)
P(1)$^{\#1}$Cd(1)P(1)	122.12(5)	P(1)Cd(1)O(2)	83.54(10)
O(1)Cd(1)O(2)$^{\#1}$	95.52(13)	O(2)$^{\#1}$Cd(1)O(2)	84.15(18)

* Symmetry transforms of equivalent atoms: $^{\#1}$ $-x + 1, y, -z + 1/2$.

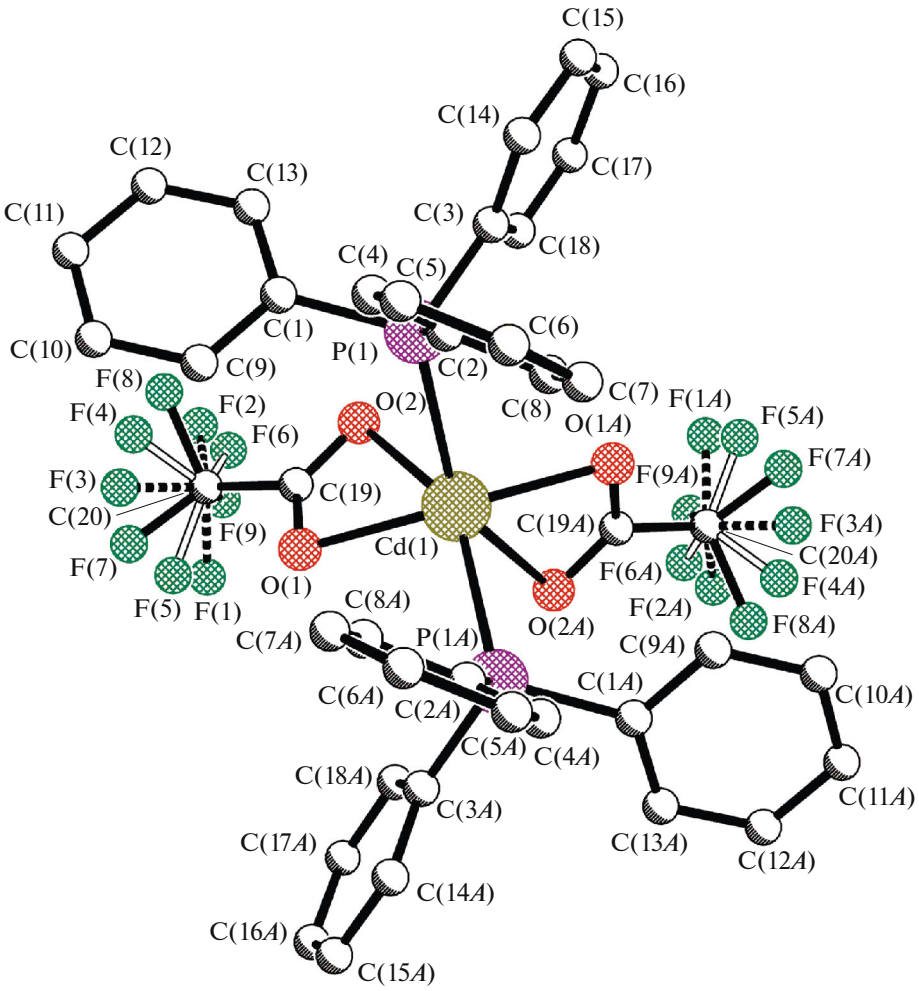

Fig. 1. Structure of molecular complex $[Cd(CF_3COO)_2(Ph_3P)_2$.

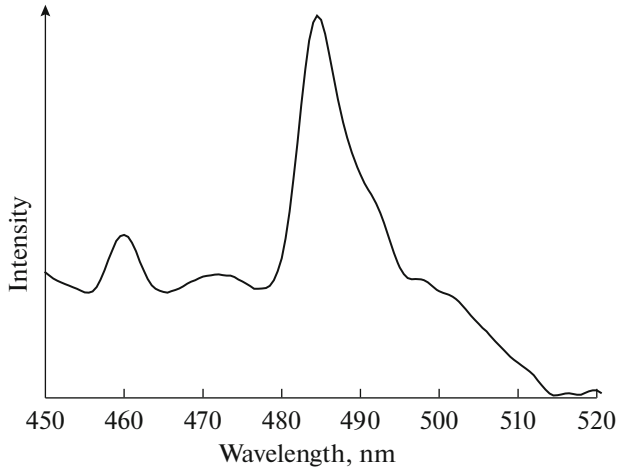

Fig. 2. PL spectrum of $[Cd(CF_3COO)_2(Ph_3P)_2$ at λ_{exc} = 230 nm.

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